

# Orthorhombic $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ ( $0.50 \leq x \leq 0.69$ ) and Monoclinic $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ ( $0.73 \leq x \leq 0.75$ ) in the System $\text{InFeO}_3\text{--In}_2\text{Ti}_2\text{O}_7$ at $1300^\circ\text{C}$ in Air

## II. Synthesis and Crystal Structures

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Two solid solutions,  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  (orthorhombic phase, *Cmcm*,  $0.50 \leq x \leq 0.69$ ) and  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  (monoclinic phase, *C2/m*,  $0.73 \leq x \leq 0.75$ ) in the pseudobinary system  $\text{InFeO}_3\text{--In}_2\text{Ti}_2\text{O}_7$  were synthesized at  $1300^\circ\text{C}$  in air. Their crystal structures which were determined by powder X-ray diffraction were closely related to those of the delafossite, (hex.) $\text{InFeO}_3$  and the pyrochlore. The crystal structural relationships between  $\text{InFeO}_3$ ,  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ , and the pyrochlore were discussed in terms of the stacking of the two-dimensional closest packed oxygen layers. The isostructural solid solutions,  $\text{In}(\text{Al}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ ,  $\text{In}(\text{Cr}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ ,  $\text{In}(\text{Ga}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ ,  $\text{In}(\text{Fe}_{1/3}\text{Ti}_{1/2}\text{Mg}_{1/6})\text{O}_{19/6}$ , and  $\text{In}(\text{Ga}_{0.30}\text{Ti}_{0.45}\text{Mg}_{0.25})\text{O}_{3.10}$  were also synthesized and their lattice constants were determined.

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**Key Words:**  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ ; pyrochlore;  $\text{InFeO}_3$ ; delafossite; two-dimensional oxygen closest packing; polytype.

## INTRODUCTION

In(III) can have a coordination number (CN) of 4, 5, 6, or 8 in oxide crystals (1). The ionic radius (with CN = 8) is in between those of Lu(III) and Sc(III) (1). Although  $\text{Lu}_2\text{Ti}_2\text{O}_7$  and  $\text{Sc}_2\text{Ti}_2\text{O}_7$  having the pyrochlore-type structure are reported (2),  $\text{In}_2\text{Ti}_2\text{O}_7$  having the pyrochlore-type and (hex.) $\text{InFeO}_3$  are not stable at 1100 and  $1300^\circ\text{C}$  in air (3, 4). In our previous papers, we reported the phase relations in the system  $\text{In}_2\text{O}_3\text{--TiO}_2\text{--Fe}_2\text{O}_3$  at  $1100^\circ\text{C}$  (3), the system

$\text{In}_2\text{O}_3\text{--TiO}_2\text{--MgO}$  at 1100 and  $1300^\circ\text{C}$  in air (4), and the conditions of synthesis and the lattice constants of the new phases,  $\text{In}(\text{A}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  (A: Al, Cr, Fe, or Ga) in the orthorhombic and/or monoclinic system (5). Hereafter, we define these compounds as Unison- $X_1$  after (3–5). Since there are incommensurate diffraction peaks along the  $b^*$  axis in both the orthorhombic and monoclinic Unison- $X_1$ , we indexed all the X-ray powder diffraction peaks that appeared in these phases using the  $h, k_1, l, k_2$ . Recently we have analyzed the averaged single-crystal structures of the orthorhombic  $\text{In}(\text{Fe}_{1/3}\text{Ti}_{2/3})\text{O}_{10/3}$  ( $a$  (Å) = 3.3504(3),  $b$  (Å) = 5.8341(7),  $c$  (Å) = 12.070(5),  $Z$  = 4, *Cmcm*) (6) and the monoclinic  $\text{In}(\text{Fe}_{0.25}\text{Ti}_{0.75})\text{O}_{3.375}$  ( $a$  (Å) = 5.9207(8),  $b$  (Å) = 3.4249(5),  $c$  (Å) = 6.3836(9), and  $\beta$  (°) = 107.96(1),  $Z$  = 2, *C2/m*) (7), while neglecting the diffraction of the satellite peaks. These crystal structures are shown in Figs. 1a and 1b). We consider that both crystal structures consist of  $\text{InO}_2^{1-}$  layers and  $(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{1+x/2}^{1+}$  layers. The In(III) is in an octahedron and both the Fe(III) and Ti(IV) are in the same crystallographic site whose CN of oxygen is 5–6. The packing orders of the two-dimensional closest oxygen layer, the mixed layer of both the cation and oxygen, and the In layer are as follows: ... In(A), O(B), [O(A, C), Fe/Ti(B)], O(B), In(A), O(C), [O(A, B), Fe/Ti(C)], O(C) and In(A)... for the orthorhombic  $\text{In}(\text{Fe}_{1/3}\text{Ti}_{2/3})\text{O}_{10/3}$  and ... In(B), O(A), [O(B, C), Fe/Ti(A)], O(A), In(C), O(B), [O(A, C), Fe/Ti(B)], O(B), In(A), O(C), [O(B, A), Fe/Ti(C)], O(C), In(B), ... for the monoclinic  $\text{In}(\text{Fe}_{0.25}\text{Ti}_{0.75})\text{O}_{3.375}$ . If  $x$  were the same in both of the crystal structures and if we neglect the displacement of the oxygen position on the ( $a, b$ ) plane (6, 7), we can consider that they are polytypic with each other.

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In the present paper, we report the conditions of synthesis of the two solid solutions,  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  (orthorhombic phase,  $Cmcm$ ,  $0.50 \leq x \leq 0.69$ ) and  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  (monoclinic phase,  $C2/m$ ,  $0.73 \leq x \leq 0.75$ ) in the pseudobinary system  $\text{InFeO}_3\text{-In}_2\text{Ti}_2\text{O}_7$  at  $1300^\circ\text{C}$  in air and the crystal structures which were determined by X-ray powder diffractometry. Finally we discuss the relationships in the crystal structures between (hex.) $\text{InFeO}_3$ , (rhomb.) $\text{InFeO}_3$ ,  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  (orthorhombic phase),  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  (monoclinic phase), the delafossite, and the pyrochlore in terms of stacking of the two-dimensional closest packed oxygen layers. The conditions of synthesis and the lattice constants of the isostructural solid solutions,  $\text{In}(\text{Al}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ ,  $\text{In}(\text{Cr}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ ,  $\text{In}(\text{Ga}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ ,  $\text{In}(\text{Fe}_{1/3}\text{Ti}_{1/2}\text{Mg}_{1/6})\text{O}_{19/6}$ , and  $\text{In}(\text{Ga}_{0.30}\text{Ti}_{0.45}\text{Mg}_{0.25})\text{O}_{3.10}$  are also reported.

### EXPERIMENTAL

Using solid-state reactions between oxide powders, we synthesized complex oxides. We used  $\text{In}_2\text{O}_3$  (99.9%),  $\text{TiO}_2$

(99.9%),  $A_2\text{O}_3$  ( $A$ : Al, Cr, Fe, or Ga) (99.9%), and  $\text{MgO}$  (99.9%) powders as starting compounds. Prior to mixing these compounds, we heated them at  $850^\circ\text{C}$  in air for 1 day. We weighed calculated amounts of the starting compounds and mixed them under ethanol in an agate mortar for about 30 min. The mixtures were pelletized (diameter, 12 mm; thickness, 1.5 mm) and heated in an alumina crucible at  $1300^\circ\text{C}$  in air for a fixed period followed by rapid cooling in air at room temperature. The furnace temperature was fixed within  $\pm 1^\circ\text{C}$ . All the specimens were then supplied to X-ray powder diffractometry for identification of phases and determination of the lattice constants. Lattice constants were calculated by the least square means method. Si powder (NBS standard reference number 640b,  $a$  ( $\text{\AA}$ ) = 5.4309) was used as the standard specimen for determining  $d$ -spacings. We repeated the process of heating and grinding the specimens until equilibrium was reached. When X-ray powder diffraction patterns show that no more change was observed, we stopped heating specimens, concluding that equilibrium was obtained. We monitored the weight of the specimens carefully before and after heating them. All the

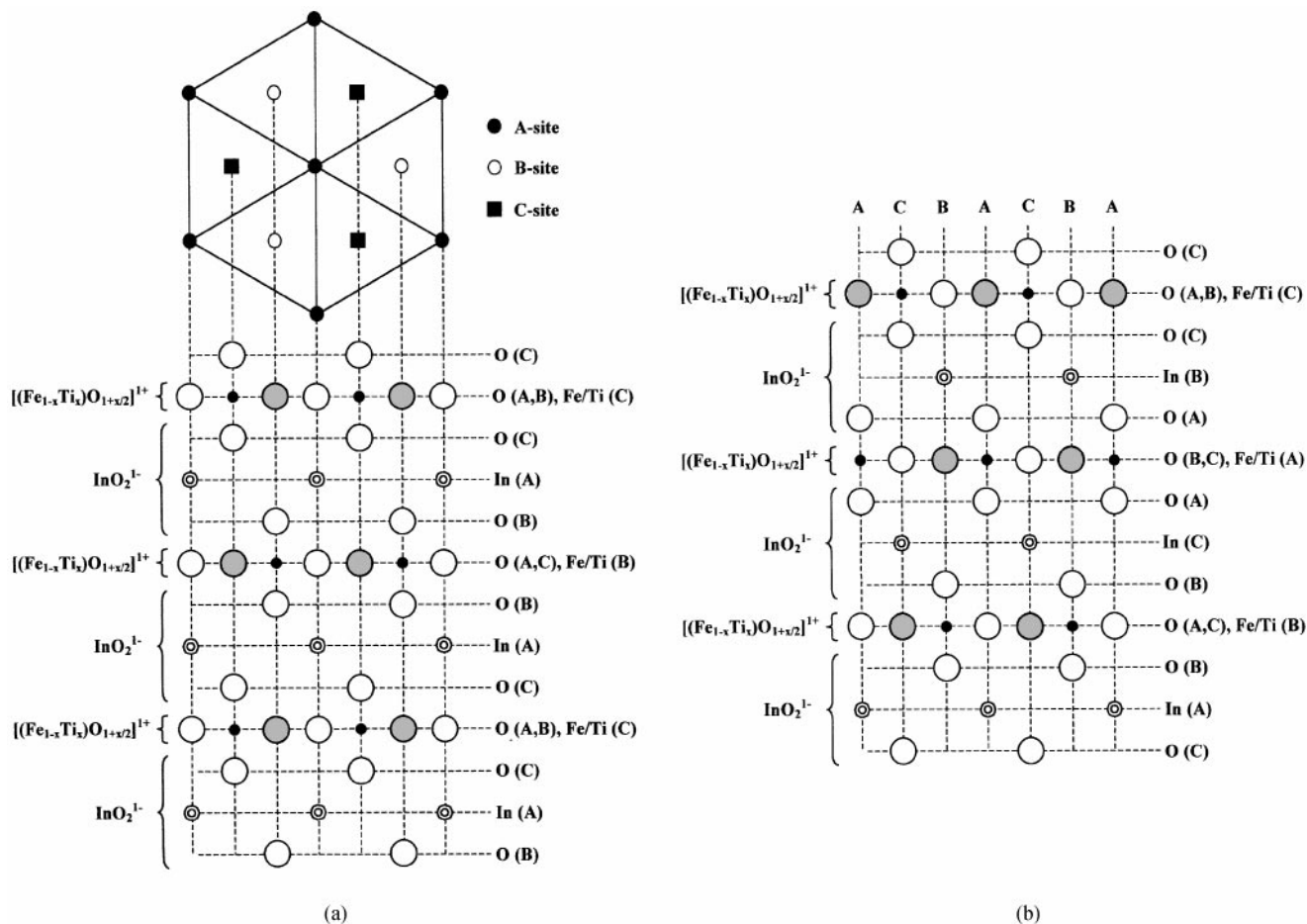


FIG. 1. (a) The crystal structure of the orthorhombic  $\text{In}(\text{Fe}_{1/3}\text{Ti}_{2/3})\text{O}_{10/3}$ . A, B, and C indicate three positions of the triangle lattice points. (b) The crystal structure of the monoclinic  $\text{In}(\text{Fe}_{0.25}\text{Ti}_{0.75})\text{O}_{3.375}$ .  $\circ$ , O;  $\bullet$ , excess oxygen;  $\odot$ , In;  $\bullet$ , Fe/Ti.

**TABLE 1**  
**The System InFeO<sub>3</sub>-In<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> at 1300°C in Air**

Mixing ratio (in a mole ratio)	Heating period (day)	Phase(s) obtained
In <sub>2</sub> O <sub>3</sub> :TiO <sub>2</sub> :Fe <sub>2</sub> O <sub>3</sub> =		
1:0:1	2 + 2	In <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub>
3:2:2	2 + 2	In <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , O
2:2:1	2 + 2	O-In(Fe <sub>0.50</sub> Ti <sub>0.50</sub> )O <sub>3.25</sub>
1:1.10:0.45	2 + 2	O-In(Fe <sub>0.45</sub> Ti <sub>0.55</sub> )O <sub>3.275</sub>
1:1.16:0.42	2 + 2	O-In(Fe <sub>0.42</sub> Ti <sub>0.58</sub> )O <sub>3.290</sub>
1:1.20:0.40	2 + 2	O-In(Fe <sub>0.40</sub> Ti <sub>0.60</sub> )O <sub>3.30</sub>
1:1.24:0.38	2 + 2	O-In(Fe <sub>0.38</sub> Ti <sub>0.62</sub> )O <sub>3.31</sub>
3:4:1	2 + 2	O-In(Fe <sub>1/3</sub> Ti <sub>2/3</sub> )O <sub>10/3</sub>
1:1.36:0.32	2 + 2	O-In(Fe <sub>0.32</sub> Ti <sub>0.68</sub> )O <sub>3.34</sub>
1:1.38:0.31	2 + 2 + 2 + 2	O-In(Fe <sub>0.31</sub> Ti <sub>0.69</sub> )O <sub>3.345</sub>
1:1.40:0.30	3 + 3 + 3	O, M
1:1.42:0.29	3 + 3 + 3	O, M
1:1.44:0.28	2 + 2 + 2	O, M
1:1.46:0.27	3 + 3 + 3	M-In(Fe <sub>0.27</sub> Ti <sub>0.73</sub> )O <sub>3.365</sub>
1:1.48:0.26	2 + 2	M-In(Fe <sub>0.26</sub> Ti <sub>0.74</sub> )O <sub>3.370</sub>
4:6:1	2 + 2	M-In(Fe <sub>0.25</sub> Ti <sub>0.75</sub> )O <sub>3.375</sub>
35:60:5	2 + 2	M, TiO <sub>2</sub> , In <sub>2</sub> TiO <sub>5</sub>
1:1:0	2 + 2	In <sub>2</sub> TiO <sub>5</sub> , TiO <sub>2</sub>

Note. O, orthorhombic phase; M, monoclinic phase.

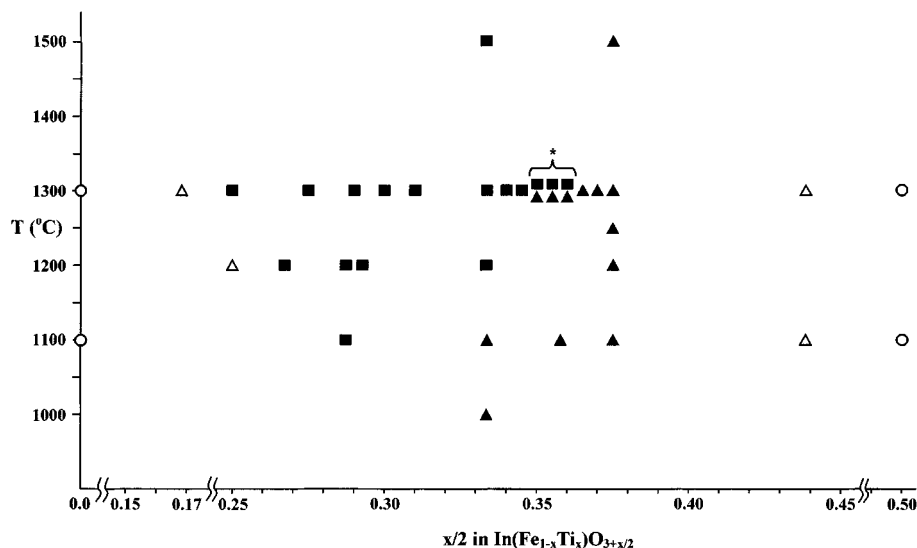
specimens obtained were well sintered. For example, the apparent density of the orthorhombic In(Fe<sub>0.50</sub>Ti<sub>0.50</sub>)O<sub>3.25</sub> in a pellet shape was 4.46 (g/cm<sup>3</sup>), namely, 74% of the  $d_x$  (the density calculated from X-ray powder data).

## RESULTS AND DISCUSSION

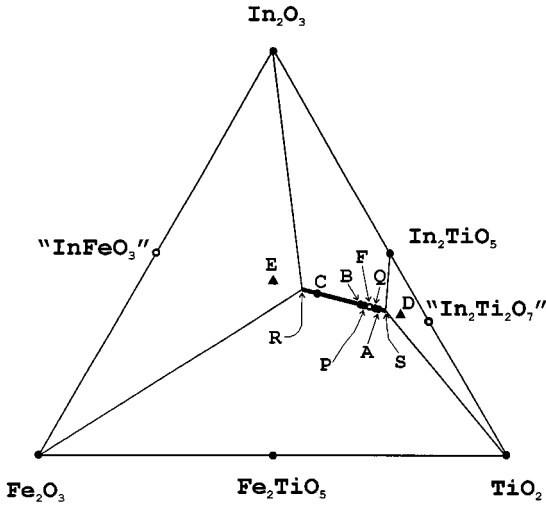
In Table 1, we show starting mixtures, heating periods, and phases obtained in the pseudobinary system InFeO<sub>3</sub>-

In<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> at 1300°C in air. We obtained an orthorhombic In(Fe<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3+x/2</sub> phase at 0.50 ≤ x ≤ 0.69 and a monoclinic In(Fe<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3+x/2</sub> phase at 0.73 ≤ x ≤ 0.75 as a single phase. The former is isostructural with the orthorhombic In(Fe<sub>1/3</sub>Ti<sub>2/3</sub>)O<sub>10/3</sub> (6) (see Fig. 1) and the latter is isostructural with the monoclinic In(Fe<sub>0.25</sub>Ti<sub>0.75</sub>)O<sub>3.375</sub> (7). At 0.69 < x < 0.73, there coexist an orthorhombic phase and a monoclinic one. We conclude that there are two solid solutions, the orthorhombic In(Fe<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3+x/2</sub> phase and the monoclinic In(Fe<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3+x/2</sub> phase in the pseudobinary system InFeO<sub>3</sub>-In<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> at 1300°C in air. In Fig. 2, we show the dependence of the stability of Unison-X<sub>1</sub> upon temperature. The orthorhombic phase is a higher temperature one and the monoclinic phase is a lower temperature one. Although the stability range of the orthorhombic phase expands at higher temperatures, the monoclinic In(Fe<sub>0.25</sub>Ti<sub>0.75</sub>)O<sub>3.375</sub> did not transform to the orthorhombic phase until its melting point (7). The monoclinic In(Fe<sub>1/3</sub>Ti<sub>2/3</sub>)O<sub>10/3</sub> exhibits a phase transformation to orthorhombic between 1100 and 1200°C. At 1100°C, reaction rate among the starting compounds was too slow to determine the stability range of the orthorhombic and the monoclinic phase exactly (3). However, it was clear that there is a region in which the two phases coexist at 1300°C. A phase diagram in the pseudobinary system InFeO<sub>3</sub>-In<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> at 1300°C in air is shown in Fig. 3. Although InFeO<sub>3</sub> and In<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> are not stable at 1300°C in air, we conclude that there are the two stable solid solutions between them.

Shannon and Prewitt reported InGaO<sub>3</sub> (high pressure form) (8) and Guiaquinta and Loye reported InMnO<sub>3</sub> (9) and InFeO<sub>3</sub> (10), which are all hexagonal phases. The crystal structure of these isostructural compounds is shown in Fig. 4a. The In(III) is in an octahedron and the Fe(III) is in



**FIG. 2.** The dependence of the crystal structure of Unison-X<sub>1</sub> in the system InFeO<sub>3</sub>-In<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> upon temperature and composition. ■, Orthorhombic phase; ▲, monoclinic phase; ○, two phases coexist; △, three phases coexist; \*, orthorhombic phase and monoclinic phase coexist. The experimental data except at 1300°C are cited from Refs. 3, 6, and 7.



**FIG. 3.** The phase relations in the pseudobinary system  $\text{InFeO}_3\text{-In}_2\text{Ti}_2\text{O}_7$  at  $1300^\circ\text{C}$  in air. ●, A single phase exists; ○, two phases coexist; ▲, three phases coexist. Both “ $\text{InFeO}_3$ ” and “ $\text{In}_2\text{Ti}_2\text{O}_7$ ” are not stable. There are two solid solutions along the line between “ $\text{InFeO}_3$ ” and “ $\text{In}_2\text{Ti}_2\text{O}_7$ .” From R to P through C and B, there is an orthorhombic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . Point F has two phases, an orthorhombic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  and a monoclinic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . Points Q to S through A, there is a monoclinic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . Chemical compositions of the points in the figure are as follows: A(4:6:1), B(3:4:1), C(2:2:1), D(35:60:5), E(3:2:2), F(1:1.42:0.29), P(0.372:0.513:0.115), and Q(0.366:0.535:0.099). The chemical compositions of R and S were not determined. Here, S(p:q:r) signifies that the chemical composition of the point S is  $\text{In}_2\text{O}_3:\text{TiO}_2:\text{Fe}_2\text{O}_3 = \text{p}:\text{q}:\text{r}$  (in a mole ratio). D has three phases,  $\text{In}_2\text{TiO}_5$ ,  $\text{TiO}_2$ , and the monoclinic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ , and E has three phases,  $\text{In}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and the orthorhombic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ .

a trigonalbipyramid. The similarity between Fig. 1a and Fig. 4a is self-evident, and they have the same layered structure except for the excess oxygen (the site occupancy, 0.59) in the  $[(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{1+x/2}]^{1+}$  layer in Fig. 1a. The crystal structure of the hypothetical (rhomb.)  $\text{InFeO}_3$  is also shown in Fig. 4b, which consists of  $\text{InO}_2^{1-}$  layers and  $\text{FeO}^{1+}$  layers with a different ordering from that in the (hex.)  $\text{InFeO}_3$ . The relationship between the (rhomb.)  $\text{InFeO}_3$  structure to the monoclinic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  in Fig. 1b, having the excess oxygen (the site occupancy, 0.68) is the same as that of (hex.)  $\text{InFeO}_3$  to the orthorhombic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . All the cations and the anions in the (hex.)  $\text{InFeO}_3$  and the (rhomb.)  $\text{InFeO}_3$  are on the trigonal lattice planes. They are considered to be polytypic with each other; however, no oxide compounds having the (rhomb.)  $\text{InFeO}_3$  structure have been reported yet. If we reasonably hypothesize that they are ionic crystals as a first approximation, we can correctly understand from the two crystal structures that the (rhomb.)  $\text{InFeO}_3$  is less stable than (hex.)  $\text{InFeO}_3$ . It is also clear that when  $x$  is small, the orthorhombic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  is more stable than the monoclinic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  and the latter is more stable than the former, when  $x$  is great. Although a com-

pound having the (rhomb.)  $\text{InFeO}_3$  type structure has not been reported yet, as we mentioned above,  $\text{In}_2\text{Se}_3$ , having the same packing order as the (rhomb.)  $\text{InFeO}_3$ , is already known in a chalcogenide system having more covalent properties (11, 12) (see Fig. 5). The crystal structure of delafossite (13) in Fig. 6 is considered to be the structure in which oxygen does not coexist on the plane of the Fe/Ti cations layer in the monoclinic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . The crystal structure of the pyrochlore,  $R_2\text{Ti}_2\text{O}_7$  ( $R$ , rare earth element; cubic system; space group,  $Fd\bar{3}m$ ; the positional parameter of oxygen is hypothesized to be  $\frac{3}{8}$ ) (14), is shown in Fig. 7, using the stacking of the  $(R_{3/4}\text{Ti}_{1/4})$  layers, the  $(R_{1/4}\text{Ti}_{3/4})$  layers and the oxygen layers. Both the  $(\frac{3}{8})R$  and  $(\frac{1}{4})\text{Ti}$  on the planes  $P_1, P_7$ , and  $P_{13}$ , the  $(\frac{1}{4})R$  and  $(\frac{3}{8})\text{Ti}$  on the planes  $P_4, P_{10}$ , and  $P_{16}$ , the oxygens on the planes  $P_2, P_6, P_8, P_{12}, P_{14}$ , and  $P_{18}$ , and both the  $(\frac{3}{8})$ oxygen and  $(\frac{1}{4})$ vacancy on the planes  $P_3, P_5, P_9, P_{11}, P_{15}$ , and  $P_{17}$  form the two-dimensional closest packing layers, respectively. If the positional parameter of the oxygen is  $\frac{3}{8}$ , all the distances between the nearest planes are identical; however, it is really greater than  $\frac{3}{8}$ , in the case of  $R_2\text{Ti}_2\text{O}_7$  (14).

**TABLE 2**

Mixing ratio (in a mole ratio)	Heating period (day)	Phase(s) obtained
A. The system $\text{InAlO}_3\text{-In}_2\text{Ti}_2\text{O}_7$ at $1300^\circ\text{C}$ in air		
$\text{In}_2\text{O}_3:\text{TiO}_2:\text{Al}_2\text{O}_3 =$		
1:0:1	1 + 1	$\text{In}_2\text{O}_3, \text{Al}_2\text{O}_3$
3:2:2	2 + 2	$\text{In}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{O}$
2:2:1	2 + 2	$\text{O-In}(\text{Al}_{0.50}\text{Ti}_{0.50})\text{O}_{3.25}$
3:4:1	2 + 2	$\text{O-In}(\text{Al}_{1/3}\text{Ti}_{2/3})\text{O}_{10/3}$
4:6:1	2 + 2	O, M
35:60:5	2 + 2	M, $\text{TiO}_2, \text{In}_2\text{TiO}_5$
1:1:0	2 + 2	$\text{In}_2\text{TiO}_5, \text{TiO}_2$
B. The system $\text{InCrO}_3\text{-In}_2\text{Ti}_2\text{O}_7$ at $1300^\circ\text{C}$ in air		
$\text{In}_2\text{O}_3:\text{TiO}_2:\text{Cr}_2\text{O}_3 =$		
1:0:1	1 + 1	$\text{In}_2\text{O}_3, \text{Cr}_2\text{O}_3$
3:2:2	2 + 2	$\text{In}_2\text{O}_3, \text{Cr}_2\text{O}_3, \text{M}$
2:2:1	2 + 2	$\text{In}_2\text{O}_3, \text{Cr}_2\text{O}_3, \text{M}$
3:4:1	2 + 2	$\text{M-In}(\text{Cr}_{1/3}\text{Ti}_{2/3})\text{O}_{10/3}$
4:6:1	2 + 2	$\text{M-In}(\text{Cr}_{0.25}\text{Ti}_{0.75})\text{O}_{3.375}$
35:60:5	2 + 2	M, $\text{TiO}_2, \text{In}_2\text{TiO}_5$
1:1:0	2 + 2	$\text{In}_2\text{TiO}_5, \text{TiO}_2$
C. The system $\text{InGaO}_3\text{-In}_2\text{Ti}_2\text{O}_7$ at $1300^\circ\text{C}$ in air		
$\text{In}_2\text{O}_3:\text{TiO}_2:\text{Ga}_2\text{O}_3 =$		
1:0:1	1 + 1	$\text{In}_2\text{O}_3, \text{Ga}_2\text{O}_3(\text{ss})$
3:2:2	2 + 2	$\text{In}_2\text{O}_3, \text{Ga}_2\text{O}_3, \text{O}$
2:2:1	2 + 2	$\text{O-In}(\text{Ga}_{0.50}\text{Ti}_{0.50})\text{O}_{3.25}$
3:4:1	2 + 2	$\text{O-In}(\text{Ga}_{1/3}\text{Ti}_{2/3})\text{O}_{10/3}$
4:6:1	2 + 2 + 2	O, M
35:60:5	2 + 2	M, $\text{TiO}_2, \text{In}_2\text{TiO}_5$
1:1:0	2 + 2	$\text{In}_2\text{TiO}_5, \text{TiO}_2$

Note. O, orthorhombic; M, monoclinic phase.

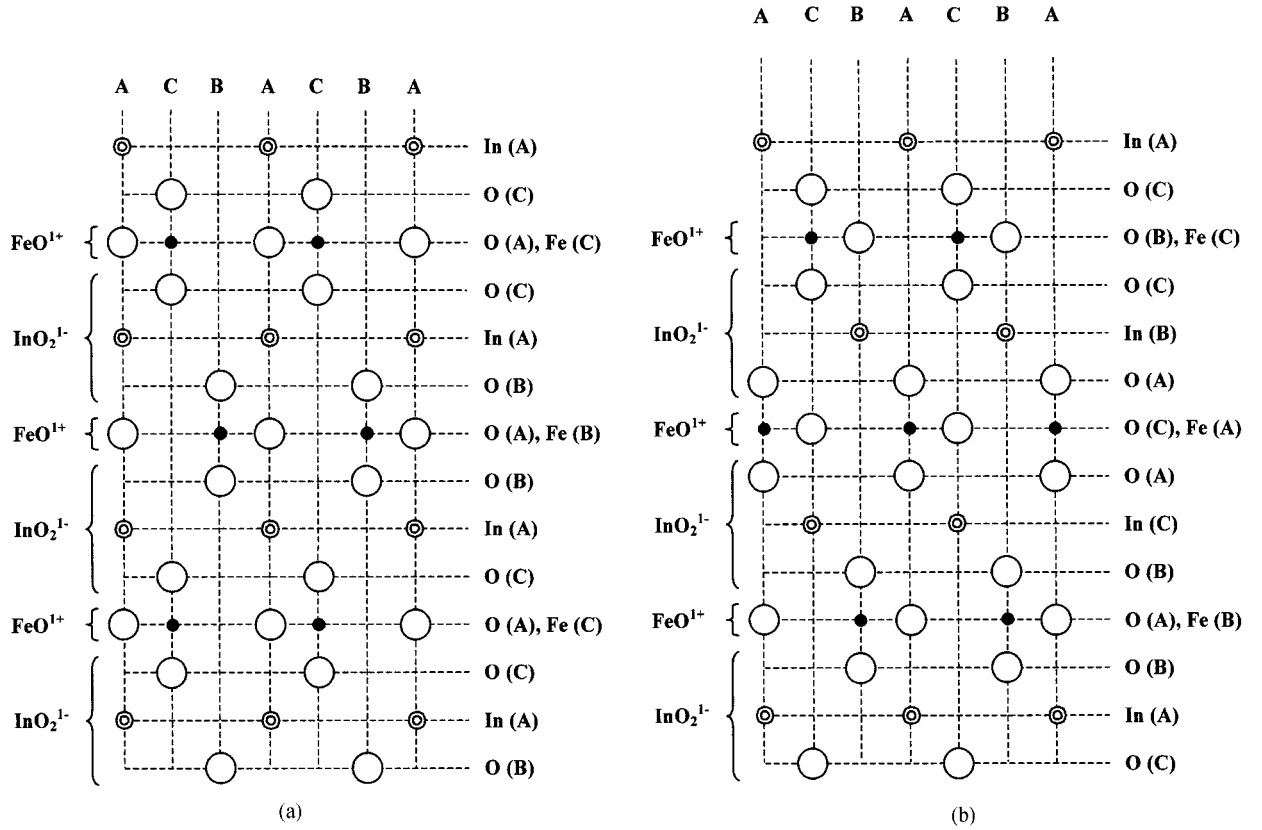


FIG. 4. (a) The crystal structure of (hex.)InFeO<sub>3</sub>, (b) The crystal structure of (rhom.)InFeO<sub>3</sub>, ○, O; ⊙, In; ●, Fe.

Therefore, the width of the  $[(R_{1/4}Ti_{3/4})O_{3/2}]^{+3/4}$ , namely the  $(R_{1/4}Ti_{3/4})$  plane sandwiched by both plane P<sub>3</sub> and plane P<sub>5</sub> (or both P<sub>9</sub> and P<sub>11</sub> or both P<sub>15</sub> and P<sub>17</sub>) is thinner than that of the hypothetical structure having  $\frac{3}{8}$ . If the width of the  $[(R_{1/4}Ti_{3/4})O_{3/2}]^{+3/4}$  layer becomes infinitesimally thin, we can conclude that the packing order of the cation and anion in the pyrochlore-type structure in Fig. 7b is the same as that in the monoclinic Unison X<sub>1</sub>. It was shown that the X-ray powder diffraction patterns of the monoclinic Unison-X<sub>1</sub> are very similar to that of Lu<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> having the pyrochlore structure (JCPDS Card 23-0375, cubic system,  $a(\text{\AA}) = 10.011$ ) (3, 5). We submitted all the X-ray powder diffraction data of the Unison-X<sub>1</sub> to the International Centre for Diffraction Data.

As we mentioned above, (hex.)InFeO<sub>3</sub> is unstable at 1100–1350°C in air; however, InFeO<sub>3</sub>(MO)<sub>m</sub> (*M*, divalent cation element; *m*, natural number) having the layered structures (see Fig. 8a in the case of *m* = 1) is stable (15). We conclude that there are at least two ways of stabilizing the unstable (hex.)InFeO<sub>3</sub> having the layer structure: (i) substituting Fe(III) in InFeO<sub>3</sub> by Ti(IV), forming In(Fe<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3+x/2</sub> with excess oxygen, or (ii) adding MO to (hex.)InFeO<sub>3</sub>, forming InFeO<sub>3</sub>(MO) in which both the Fe(III) and the *M*(II) occupy the same crystallographic

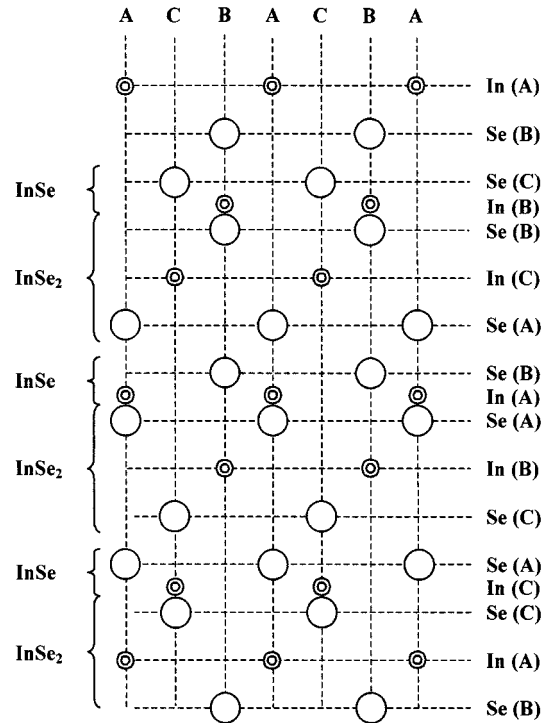


FIG. 5. The crystal structure of (rhom.)In<sub>2</sub>Se<sub>3</sub>, ○, Se; ⊙, In.

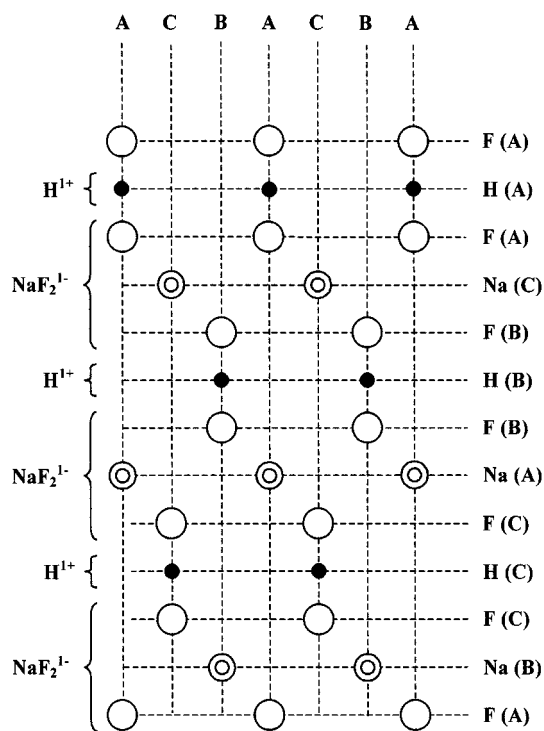


FIG. 6. The crystal structure of delafossite.  $\circ$ , F;  $\odot$ , Na;  $\bullet$ , H.

position in the trigonal bipyramidal layers of  $(\text{FeM})\text{O}_2^{1+}$ . O and Fe/M in the  $(\text{FeM})\text{O}_2^{1+}$  are almost on the same two-dimensional plane (15). Although there is no compound in the oxide system which could be formed from both (rhomb.) $\text{InFeO}_3$  and  $\text{MO}$ , there is  $\text{InGaS}_3(\text{ZnS})$  (see Fig. 8b) in the sulfide system having the same packing order (11, 12). We think it is quite reasonable to assume that the chemical bonding property in sulfides is more covalent than in oxides. Although there exist compounds  $(\text{InGaS}_3)_n(\text{ZnS})_m$  ( $n, m$ : natural numbers) in the system  $\text{In}_2\text{S}_3\text{-Ga}_2\text{S}_3\text{-ZnS}$  (11, 12), whose packing orderings are different from each other, there was no polytype in the system  $\text{InAO}_3(\text{ZnO})_m$  ( $A$ : Al, Fe, or Ga) (16, 17, and 18), because of the ionic property. In the present system,  $\text{In}_2\text{O}_3\text{-TiO}_2\text{-A}_2\text{O}_3$ , there is no polytype; however, we conclude that there are two phases, the orthorhombic  $\text{In}(\text{A}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  and the monoclinic  $\text{In}(\text{A}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ , which we think have the relationship of "extended" (or pseudo-) polytype with each other, if the coexistence region of the two phases is infinitesimally narrow.

In the system  $\text{In}_2\text{O}_3\text{-TiO}_2\text{-A}_2\text{O}_3$  ( $A$ : Al, Cr, or Ga) at  $1300^\circ\text{C}$  in air, we synthesized  $\text{In}(\text{A}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ , which is isostructural with the orthorhombic and/or monoclinic  $\text{In}(\text{Fe}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . Tables 2A, 2B, and 2C show mixing

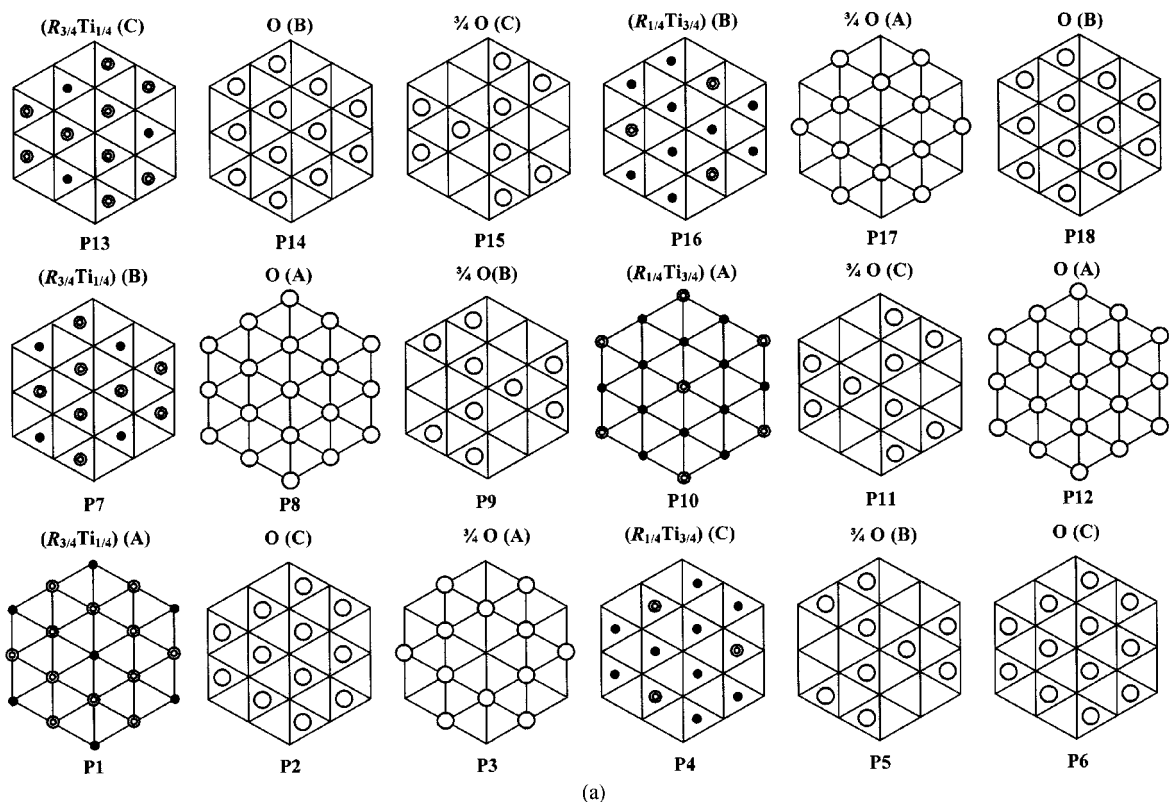


FIG. 7. The crystal structure of the  $\text{R}_2\text{Ti}_2\text{O}_7$  having the pyrochlore-type structure. (a)  $\circ$ , O;  $\odot$ , R;  $\bullet$ , Ti. A, B, and C indicate three positions of the triangle lattice points. (b)  $\circ$ , O(100%);  $\odot$ , O( $\frac{2}{3}$ );  $\odot$ , R(100%);  $\odot$ , ( $\frac{1}{2}\text{R} + \frac{1}{2}\text{Ti}$ );  $\bullet$ , Ti(100%).

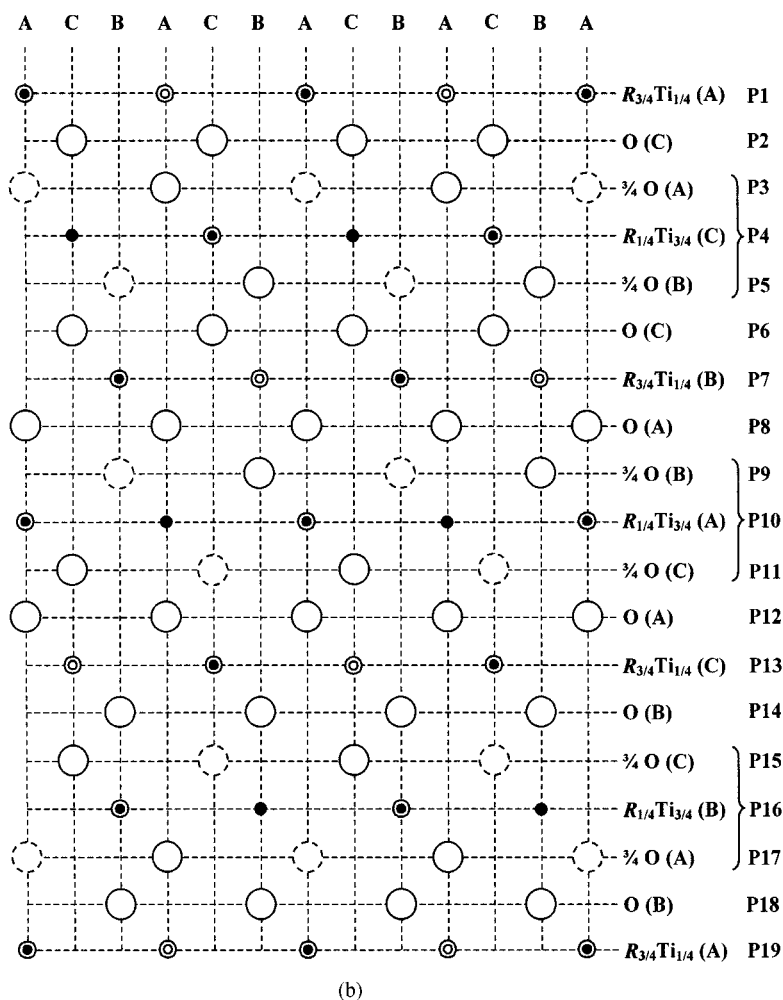


FIG. 7—Continued

ratios of starting mixtures, heating periods, and phases obtained in these systems. In Table 3A, we show the lattice constants of the  $\text{In}(\text{A}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  phases. Figures 9a, 9b,

and 9c show that phase relations in the pseudobinary system  $\text{InAO}_3\text{--In}_2\text{Ti}_2\text{O}_7$  at  $1300^\circ\text{C}$  in air. In the pseudobinary system  $\text{InAO}_3\text{--In}_2\text{Ti}_2\text{O}_7$  ( $A = \text{Al}$  or  $\text{Ga}$ ), there are two solid

**TABLE 3A**  
Lattice Constants of Compounds in the System  $\text{In}_2\text{O}_3\text{--TiO}_2\text{--A}_2\text{O}_3$  ( $A$ : Fe, Al, Cr, or Ga) at  $1300^\circ\text{C}$  in Air

Compound	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)	$q$	$V$ (Å <sup>3</sup> )
$\text{In}(\text{Fe}_{0.50}\text{Ti}_{0.50})\text{O}_{3.25}$	5.8936(6)	3.3684(3)	12.154(1)		0.277	241.3
$\text{In}(\text{Fe}_{1/3}\text{Ti}_{2/3})\text{O}_{10/3}$	5.909(1)	3.3614(6)	12.123(4)		0.333	241.2
$\text{In}(\text{Fe}_{0.25}\text{Ti}_{0.75})\text{O}_{3.375}$	5.9192(6)	3.3837(4)	6.3715(7)	108.09(1)	0.362	121.3
$\text{In}(\text{Al}_{0.50}\text{Ti}_{0.50})\text{O}_{3.25}$	5.8359(6)	3.3837(9)	12.098(2)		0.270	241.3
	3.3698(6) <sup>a</sup>		12.100(2) <sup>a</sup>			
$\text{In}(\text{Al}_{1/3}\text{Ti}_{2/3})\text{O}_{10/3}$	5.833(3)	3.3710(2)	12.060(6)		0.353	237.1
$\text{In}(\text{Cr}_{1/3}\text{Ti}_{2/3})\text{O}_{10/3}$	5.9246(8)	3.3562(5)	6.3546(9)	108.10(1)	0.341	120.1
$\text{In}(\text{Cr}_{0.25}\text{Ti}_{0.75})\text{O}_{3.375}$	5.9253(5)	3.3704(3)	6.3512(6)	108.09(1)	0.371	121.3
$\text{In}(\text{Ga}_{0.50}\text{Ti}_{0.50})\text{O}_{3.25}$	5.835(1)	3.3787(7)	12.104(2)		0.284	238.6
$\text{In}(\text{Ga}_{1/3}\text{Ti}_{2/3})\text{O}_{10/3}$	5.851(1)	3.3890(7)	12.057(3)		0.330	239.1

Note. For a definition of  $q$ , see Refs. (3–5).

<sup>a</sup>The lattice constants in hexagonal system. The data of  $\text{In}(\text{Al}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  are cited from (5).

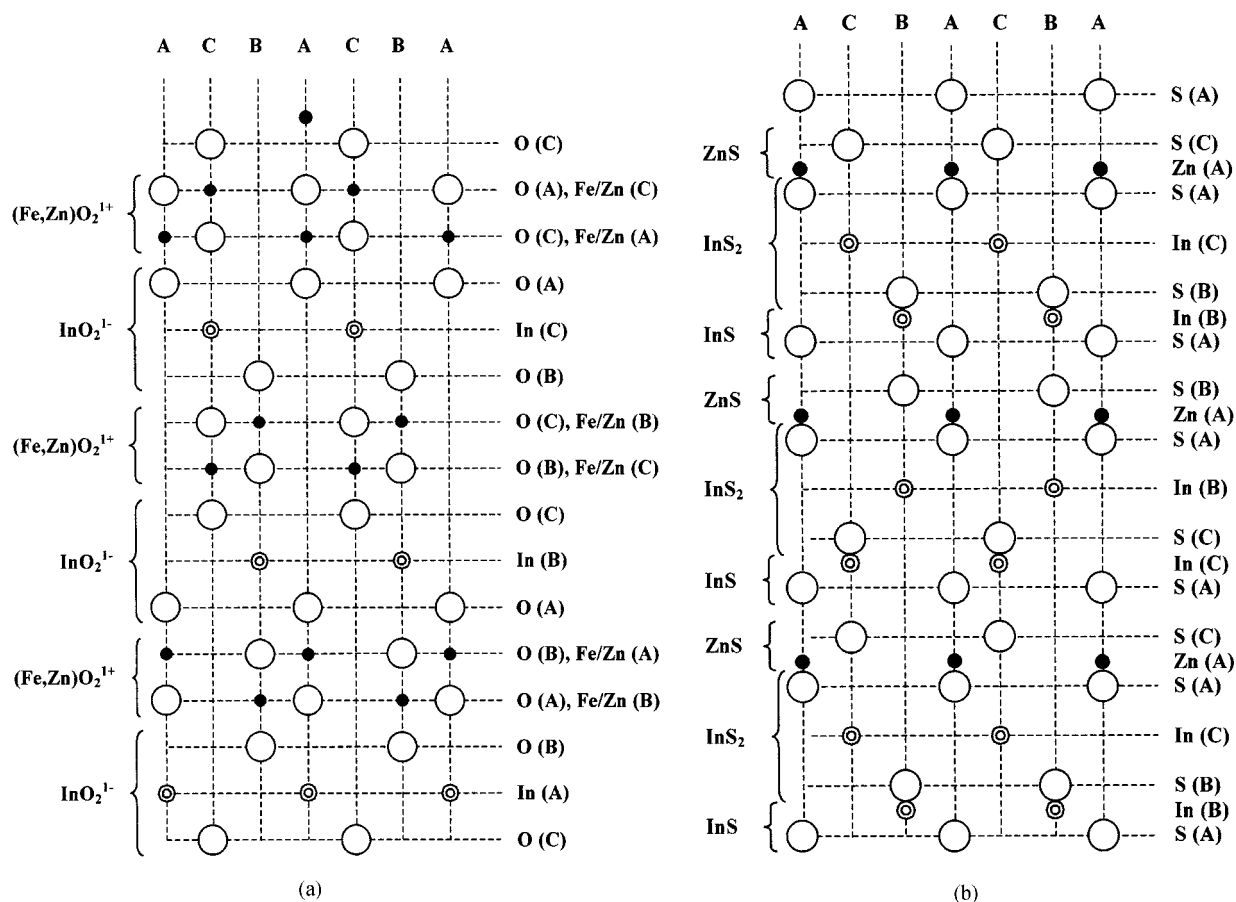


FIG. 8. (a) The crystal structure of  $\text{InFeO}_3(\text{ZnO})$ .  $\circ$ , O;  $\odot$ , In;  $\bullet$ , Fe/Zn. (b) The crystal structure of  $\text{In}_2\text{ZnS}_4$  (IIb).  $\circ$ , S;  $\odot$ , In;  $\bullet$ , Zn.

solutions as in the system  $\text{InFeO}_3\text{-In}_2\text{Ti}_2\text{O}_7$ ; however, there is no orthorhombic  $\text{In}(\text{Cr}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  in the system  $\text{InCrO}_3\text{-In}_2\text{Ti}_2\text{O}_7$ . We cannot define exactly the CN of the  $(\text{Cr}_{1-x}\text{Ti}_x)$  cations in both structures because of the incommensurate structures; however, we can safely conclude that the CN of the cations  $(\text{Cr}_{1-x}\text{Ti}_x)$  in the monoclinic phase is greater than that of the orthorhombic phase. If we consider the strong site preference effect of the Cr(III) in oxide crystals which prefers CN = 6, it is reasonable that there is only a monoclinic phase in the system. However, since Al, Fe, or Ga take CN = 4, 5, and 6 together

with Ti(IV), there exist both phases in the system  $\text{In}_2\text{O}_3\text{-TiO}_2\text{-Al}_2\text{O}_3$  or in the system  $\text{In}_2\text{O}_3\text{-TiO}_2\text{-Ga}_2\text{O}_3$ .

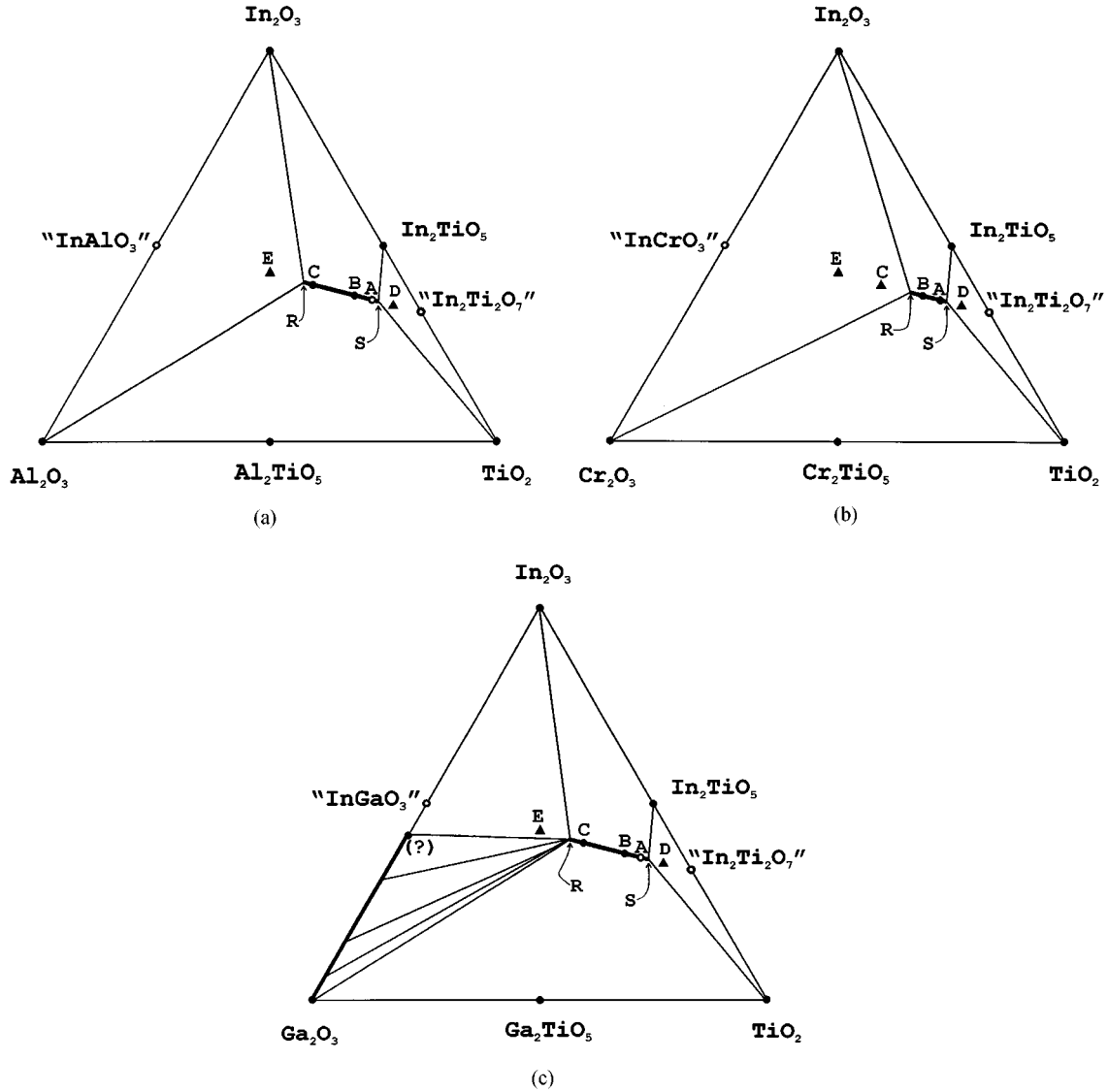
In the systems  $\text{In}_2\text{O}_3\text{-TiO}_2\text{-Fe}_2\text{O}_3\text{-MgO}$  and  $\text{In}_2\text{O}_3\text{-TiO}_2\text{-Ga}_2\text{O}_3\text{-MgO}$  at  $1300^\circ\text{C}$  in air, we synthesized  $\text{In}(\text{Fe}_{1/3}\text{Ti}_{1/2}\text{Mg}_{1/6})\text{O}_{19/6}$  and  $\text{In}(\text{Ga}_{0.30}\text{Ti}_{0.45}\text{Mg}_{0.25})\text{O}_{3.10}$ , which are orthorhombic phases. We conclude that Mg(II) forms the orthorhombic Unison- $X_1$  structure together with both Ti(IV) and Fe(III) (or Ga(III)). We show the condition of synthesis and the lattice constants of  $\text{In}(\text{Fe}_{1/3}\text{Ti}_{1/2}\text{Mg}_{1/6})\text{O}_{19/6}$  and  $\text{In}(\text{Ga}_{0.30}\text{Ti}_{0.45}\text{Mg}_{0.25})\text{O}_{3.10}$  in Table 3B.

TABLE 3B  
Condition of Synthesis and Lattice Constants of Compounds in the System  $\text{In}_2\text{O}_3\text{-TiO}_2\text{-Fe}_2\text{O}_3$  (or  $\text{Ga}_2\text{O}_3$ )-MgO at  $1300^\circ\text{C}$  in Air

Compound	Heating period (day)	$a$ ( $\text{\AA}$ )	$b$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )	$q^*$	$V$ ( $\text{\AA}^3$ )
$\text{In}(\text{Fe}_{1/3}\text{Ti}_{1/2}\text{Mg}_{1/6})\text{O}_{19/6}$	1	5.907(1)	3.3753(6)	12.153(2)	—	242.3
$\text{In}(\text{Ga}_{0.30}\text{Ti}_{0.45}\text{Mg}_{0.25})\text{O}_{3.10}$	1	5.858(1)	3.3933(7)	12.102(3)	—	240.6

Note.  $q$  could not be determined.





**FIG. 9.** (a) Two solid solutions in the pseudobinary system  $\text{InAlO}_3\text{-In}_2\text{Ti}_2\text{O}_7$  at  $1300^\circ\text{C}$  in air. ●, A single phase exists; ○, two phases coexist; ▲, three phases coexist. “ $\text{InAlO}_3$ ” is not stable. There are two solid solutions along the line between “ $\text{InAlO}_3$ ” and “ $\text{In}_2\text{Ti}_2\text{O}_7$ ”. The point A has two solid solutions, an orthorhombic  $\text{In}(\text{Al}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  and a monoclinic  $\text{In}(\text{Al}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . The coexistence range of the two phases is very narrow as in the system  $\text{InFeO}_3\text{-In}_2\text{Ti}_2\text{O}_7$ . From R to the very neighborhood of the point A through C and B, there is an orthorhombic  $\text{In}(\text{Al}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  and from the very neighborhood of point A to S, there is a monoclinic  $\text{In}(\text{Al}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . Point D has three phases,  $\text{In}_2\text{TiO}_5$ ,  $\text{TiO}_2$ , and the monoclinic  $\text{In}(\text{Al}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ , and point E has three phases,  $\text{In}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and the orthorhombic  $\text{In}(\text{Al}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . Chemical composition of the points are as follows: A(4:6:1), B(3:4:1), C(2:2:1), D(35:60:5), and E(3:2:2). The chemical composition of R and S were not determined. Here, S(p:q:r) signifies that the chemical composition of the point S is  $\text{In}_2\text{O}_3\text{:TiO}_2\text{:Al}_2\text{O}_3 = \text{p:q:r}$  (in a mole ratio). (b) A solid solution in the pseudobinary system  $\text{InCrO}_3\text{-In}_2\text{Ti}_2\text{O}_7$  at  $1300^\circ\text{C}$  in air. ●, A single phase exists; ○, two phases coexist; ▲, three phases coexist. “ $\text{InCrO}_3$ ” is not stable. Along the line between “ $\text{InCrO}_3$ ” and “ $\text{In}_2\text{Ti}_2\text{O}_7$ ” there is a monoclinic  $\text{In}(\text{Cr}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  solid solution from R to S. D has three phases,  $\text{In}_2\text{TiO}_5$ ,  $\text{TiO}_2$ , and the monoclinic  $\text{In}(\text{Cr}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . The points C and E have three phases  $\text{In}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and the monoclinic  $\text{In}(\text{Cr}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . The chemical composition of A, B, C, D, E, R, and S are as follows: A(4:6:1), B(3:4:1), C(2:2:1), D(35:60:5), E(3:2:2), R(?), and S(?). Here, S(p:q:r) signifies that the chemical composition of the point S is  $\text{In}_2\text{O}_3\text{:TiO}_2\text{:Cr}_2\text{O}_3 = \text{p:q:r}$  (in a mole ratio). (c) Two solid solutions in the pseudobinary system  $\text{InGaO}_3\text{-In}_2\text{Ti}_2\text{O}_7$  at  $1300^\circ\text{C}$  in air. “ $\text{InGaO}_3$ ” is not stable. There is a solid solution of  $\text{Ga}_2\text{O}_3(\text{ss})$  from  $\text{Ga}_2\text{O}_3$  to the vicinity of “ $\text{InGaO}_3$ ”. There are two solid solutions along the line between “ $\text{InGaO}_3$ ” and “ $\text{In}_2\text{Ti}_2\text{O}_7$ ”. From R to the very neighborhood of the point A through B and C, there is an orthorhombic  $\text{In}(\text{Ga}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$  and from the very neighborhood of the point A to S, there is a monoclinic  $\text{In}(\text{Ga}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . There is a narrow range of coexistence of the two phases at the point A. The chemical composition of A, B, C, D, E, R, and S are as follows: A(4:6:1), B(3:4:1), C(2:2:1), D(35:60:5), E(3:2:2), R(?), and S(?). Here, S(p:q:r) signifies that the chemical composition of the point S is  $\text{In}_2\text{O}_3\text{:TiO}_2\text{:Ga}_2\text{O}_3 = \text{p:q:r}$  (in a mole ratio). D has three phases,  $\text{In}_2\text{TiO}_5$ ,  $\text{TiO}_2$ , and the monoclinic  $\text{In}(\text{Ga}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ . E has three phases,  $\text{In}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3(\text{ss})$ , and the orthorhombic  $\text{In}(\text{Ga}_{1-x}\text{Ti}_x)\text{O}_{3+x/2}$ .

We are in a process of synthesizing the isostructural compounds in the system  $R_2O_3$ - $TiO_2$ - $A_2O_3$  ( $R$ , rare earth element) with Unison- $X_1$  structure at elevated temperatures. We conclude that there is a family of compounds,  $R(A_{1-x}Ti_x)O_{3+x/2}$  in the system  $R_2O_3$ - $TiO_2$ - $A_2O_3$  ( $R$ , rare earth element),  $In(A_{1-x}Ti_x)O_{3+x/2}$  in the  $In_2O_3$ - $TiO_2$ - $A_2O_3$ , and  $In_{12/13}Ti_{12/13}B_{2/13}O_{44/13}$  in the system  $In_2O_3$ - $TiO_2$ - $BO$ , at elevated temperatures which belongs to the crystal structure of the orthorhombic  $In(Fe_{1-x}Ti_x)O_{3+x/2}$  or the monoclinic  $In(Fe_{1-x}Ti_x)O_{3+x/2}$ . The crystal structure analysis for the orthorhombic  $In(Fe_{1/3}Ti_{2/3})O_{10/3}$  including the satellite diffraction peaks is also in progress (19).

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